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^{13}C NUCLEAR MAGNETIC RESONANCE IN GRAPHITE INTERCALATION COMPOUNDS

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ABSTRACT

The ^{13}C NMR chemical shifts of graphite intercalation compounds have been calculated. For acceptor types, the shifts come mainly from the paramagnetic (Ramsey) intra-atomic terms. They are related to the gross features of the two-dimensional band structures. The calculated anisotropy is about -140 ppm and is independent of the finer details such as charge transfer. For donor types, the carbon $2p\pi$ orbitals are spin-polarized because of mixing with metal conduction electrons, thus there is an additional dipolar contribution which may be correlated with the electronic specific heat. The general agreement with experimental data is satisfactory.

A wide variety of molecular and metallic species may be intercalated between the carbon layers of graphite. Because of the high electrical conductivities and the nearly two-dimensional characteristics, these graphite intercalation compounds (GIC) have been extensively studied.[1,2] From the ^{13}C nuclear magnetic resonance (NMR) spectra, the chemical shifts (CS) may be used as microscopic probes for the electronic structures. The method is also universally applicable to GIC of both the acceptor (with molecular species such as Br_2, HNO_3, AsF_5, $SbCl_5$, $AlCl_3$, etc.) and donor (with metallic species such as K, Cs, etc.) types. The pristine graphite itself has a layered structure with relatively weak interplanar interactions. Following the standard notations of the coordinate systems[3], the planes of the carbon atoms are parallel to the xy-planes and the z-axis is a threefold symmetry axis. The ^{13}C CS-tensor δ is expected to be both diagonal and axially symmetric ($-\delta$ is often denoted as the chemical shift shielding parameter σ in the literature).[4-7] The diagonal components δ_{zz}, δ_{xx}, and δ_{yy} will be abbreviated as δ_z, δ_x, and δ_y. Since $\delta_x = \delta_y$, there are only two independent components, δ_z and δ_x, which may be measured experimentally with the magnetic field $\underset{\sim}{B}$ parallel and perpendicular to the z-axis. They will be expressed in ppm (10^{-6}) with respect to tetramethylsilane (TMS) as the reference. It is convenient to define $\delta_i = (\delta_z + 2\delta_x)/3$ and $\delta_a = \delta_z - \delta_x$ as the isotropic and anisotropic parts of the CS. While structural changes do occur upon intercalation, the carbon layer structures remain intact for GIC, hence we also expect their CS tensor to have approximate axial symmetry.

There are experimental difficulties of ^{13}C NMR due to the low natural abundances (1%) of ^{13}C isotopes, unfavorable relaxation times, etc. Despite these difficulties, the general features of the experimental CS are now known.[8-16] Because large single crystals of graphite are not readily available, many GIC samples are prepared by intercalation into highly oriented pyrolytic graphite (HOPG) which is polycrystalline with the z-axis of individual crystallites in good mutual alignment throughout the specimen ($\sim 2^o$ spread), though the x- and y-axes, in the graphite planes, are disordered from crystallite to crystallite. For these GIC samples derived from HOPG, sharp resonance lines are usually observed when $\underset{\sim}{B}$ is perpendicular to the z-axis. Although structural changes do occur during intercalation[2], these experimental evidences ($\delta_x = \delta_y$) indicate that the axial symmetry of the CS tensor about the z-axis is indeed retained. Also, nearly universal values of $\delta_z \sim 40$ and $\delta_x \sim 180$ have been observed for all GIC of acceptor type (GICA); these shifts are nearly independent of the GICA composition. On the contrary, both δ_z and δ_x vary with the compositions of the GIC of donor types (GICD).

In the present work, we have calculated the CS for GIC and have considered the "band" and the "dipolar" contributions. We will show that the former term depends only on the gross features of the electronic $2p\sigma$ and $2p\pi$ band structures and is not very sensitive toward the finer details such as charge transfers or Fermi levels. We will then correlate the "dipolar" term with the electronic specific heat of GIC. It will then be shown that only "band" contribution may be present for GICA

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(since their electronic specific heats are very small) but both terms may be important for GICD.

We will first consider the "band" contribution. The main contribution to CS comes from the paramagnetic (Ramsey) intra-atomic term[4-7] while the diamagnetic term (Lamb) may be neglected because it is both small and nearly isotropic. For molecules, the Ramsey term of CS is due to the deviations from spherical symmetry of the electronic charge distribution[4,5] and may be calculated from the interaction between the occupied and empty molecular orbitals. For solids, the molecular orbitals are replaced by Bloch functions, thus we have[17-19]

$$\delta_z = (2e^2\hbar^2/m^2c^2)\langle r^{-3}\rangle_{2p} \Sigma_v \left[\Sigma_c (E_c - E_v)^{-1} \langle \psi_v | L_z | \psi_c \rangle \langle \psi_c | L_z | \psi_v \rangle \right]$$

(1)

where the factor of 2 is included for up and down spins, c is light velocity, $\hbar$ is Planck's constant divided by 2π, e and m are electronic charge and mass, L_z is the z-component of angular momentum operator in units of $\hbar$, $\langle r^{-3}\rangle_{2p}$ is the expectation value of the inverse cube distance for the carbon 2p-orbitals, ψ and E are the wave functions and their energies.

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The subscripts v and c refer to valence (occupied) and conduction (unoccupied or excited) states. The functions ψ_v and ψ_c inside the square bracket have the same wave vector $\underset{\sim}{k}$. $\sum_c$ refers to summation over the discrete excited states. $\sum_v$ refers to integration or average over the $\underset{\sim}{k}$-space or Brillouin zone (BZ). Following Strong etal.[17], a reasonable choice of $\langle r^{-3} \rangle_{2p}$ is $1.8a_o^{-3} = 12.2 \, \text{Å}^{-3}$ for carbon 2p-orbitals where a_o is the Bohr radius of the hydrogen atom, hence $(2e^2 \hbar^2/m^2 c^2) \langle r^{-3} \rangle_{2p} = 5200$ ppm when $E_c - E_v$ is expressed in units of eV. The expression for δ_x is rather similar with L_z replaced by L_x.

Usually, informations are rather incomplete about the excited states, thus the energy denominators in (1) are often replaced by an average excitation energy ΔE so that the closure relation may be used.[4,5] However, the choice of ΔE is somewhat arbitrary. For anisotropic solids such as graphite, there would be even more uncertainty in choosing two arbitrary values for δ_z and δ_x.

Since CS would depend only on the general features of the energy bands, it may be suffice to use the tight-binding approximation for two-dimensional graphite where the wave functions of the valence state and the first excited state have been given by Lomer.[3] This limited information about the valence state ψ_v, E_v and the first excited state (subscript c=1) ψ_1, E_1 (the lowest unoccupied state that satisfies the condition $\langle \psi_v | L | \psi_1 \rangle = 0$) permits us to give an over-estimate and under-estimate of CS:

(a) We may replace the energy denominator $E_c - E_v$ in (1) by the common value $\Delta E_1 = E_1 - E_v$. Using the closure relation,

we get:

$$\delta_z = 5200 \sum_v (\Delta E_1)^{-1} \langle \psi_v | L_z^2 | \psi_v \rangle \qquad (2)$$

We will refer to (2) as the average energy (AE) approximation. Clearly, AE is an over-estimate since ΔE_1 is the lowest possible value of $E_c - E_v$ and all terms in the square bracket of (1) are positive. The equation is similar (with L_z replaced by L_x) for δ_x. However, a different value of ΔE_1 must be used.

(b) We may truncate the series in (1) by including ψ_1 only under $\sum_c$:

$$\delta_z = 5200 \sum_v (\Delta E_1)^{-1} |\langle \psi_v | L_z | \psi_1 \rangle|^2 \qquad (3)$$

We will refer to (3) as the first excited state (FE) approximation. Clearly, FE is an under-estimate since all terms in (1) are positive.

Because of the reflection symmetry in the xy-plane of graphite, the π-states are based entirely on the atomic $2p_z$ (denoted as p_0, where the subscript 0 refers to the azimuthal quantum number) functions of the carbon atom, whereas the σ-states are based entirely on the atomic 2s, $2p_{+1}$ and $2p_{-1}$ (abbreviated as s, p_+, p_-) functions. Except for a small region near the center Γ of the BZ, the states are arranged from lower to higher energies in the order of σ, π (unprimed denotes valence or occupied orbitals), π', σ' (primed denotes conduction or unoccupied orbitals).[20-22] The selection rules are $\sigma\pi'$, $\pi\sigma'$ for δ_x and $\sigma\sigma'$ for δ_z, thus the denominator

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ΔE_1 is smaller in the former case. From either (2) or (3), it follows that $\delta_x > \delta_z$ or $\delta_a < 0$ which is in accordance with the experimental results for GIC of acceptor type.

At the center Γ of the BZ, there is no mixing between the s and p-functions.[3] The pure s-functions are omitted here because they do not contribute to CS. The occupied states are $\sigma_\pm = (p_{A\pm} + p_{Bx})/2^{\frac{1}{2}}$ (twofold degnerate) and $\pi = (p_{A0} + p_{B0})/2^{\frac{1}{2}}$ where subscript A and B refer to the two atoms in the unit cell, $\pm$ and 0 refer to the azimuthal quantum number $m = \pm 1, 0$ of the atomic 2p-functions. Similarly, the unoccupied states are $\sigma_\pm' = (p_{A\pm} - p_{B\pm})/2^{\frac{1}{2}}$ (twofold degenerate) and $\pi' = (p_{A0} - p_{B0})/2^{\frac{1}{2}}$. The atoms A and B have the same CS, hence it is suffice to use L_{zA} and L_{xA}. For L_{zA}, the only nonzero matrix elements are the diagonal elements $\langle p_{A\pm}|L_{zA}|p_{A\pm}\rangle$, thus the $\sigma_+ \sigma_+'$ and $\sigma_- \sigma_-'$ excitations would contribute to δ_z. In the AE approximation, we have

$$\delta_z = (2)(5200)\langle \sigma_+ |L_{zA}^2|\sigma_+\rangle/(E_\sigma'-E_\sigma) = 5200/(E_\sigma'-E_\sigma) \qquad (4)$$

On the other hand, the FE approximation is smaller by a factor of 2,

$$\delta_z = (2)(5200)|\langle \sigma_+ | L_{zA}| \sigma_+'\rangle|^2/(E_\sigma'-E_\sigma) = 2600/(E_\sigma'-E_\sigma) \qquad (5)$$

Similarly, the $\sigma_\pm \pi'$ and $\pi \sigma_\pm'$ excitations would contribute to δ_x. In the AE approximation, we nave

$$\delta_x = (5200)\left[2(E_\pi'-E_\sigma)^{-1}\langle \sigma_+|L_{xA}^2|\sigma_+\rangle + (E_\sigma'-E_\pi)^{-1}\langle \pi|L_{xA}^2|\pi\rangle\right]$$
$$= 2600\left[(E_\pi'-E_\sigma)^{-1} + (E_\sigma'-E_\pi)^{-1}\right] \qquad (6)$$

Again, the FE approximation is smaller by a factor of 2,

$$\delta_x = 5200)\left[2(E_\pi'-E_\sigma)^{-1}|\langle \sigma_+|L_{xA}|\pi'\rangle|^2 + 2(E_\sigma'-E_\pi)^{-1}|\langle \pi|L_{xA}|\sigma_+'\rangle|^2\right]$$
$$= 1300\left[(E_\pi'-E_\sigma)^{-1} + (E_\sigma'-E_\pi)^{-1}\right] \qquad (7)$$

Energy band calculations[20, 21] give $E_\sigma' - E_\sigma = 12$ eV,
$E_\pi'-E_\sigma=E_\sigma'-E_\pi= 15$ eV. For center Γ, we get $\delta_z=433$, $\delta_x=347$,
$\delta_a = \delta_z-\delta_x=86$ in the AE approximation and $\delta_z=216$, $\delta_x=174$,
$\delta_a=42$ in the FE approximation.

We will now calculate CS at one of the corners P of the
BZ. We have the same π and π' wave functions as before,
and $E_\pi = E_{\pi'}$. There are now two σ-functions. One of them,
denoted as σ_1, is twofold degenerate and is a mixture of s
and p-functions. The other, denoted as σ_2, is a pure
p-function. Similarly, there are the unoccupied σ_1' and
σ_2' states. In the order of increasing energies, the σ and σ'
functions and their energies are[3]:

$$E_1=\tfrac{1}{2}(E_s+E_p)-\tfrac{1}{2}\left[(E_s-E_p)^2+36H_{sp}^2\right]^{\tfrac{1}{2}}, \quad \sigma_1=\alpha s_B+\beta p_{A+}, \quad \alpha s_A+\beta p_{B-}.$$

$$E_2=E_p+3H_{pp}', \quad \sigma_2=(p_{A-}+p_{B+})/2^{\tfrac{1}{2}}.$$

$$E_1'=\tfrac{1}{2}(E_s+E_p)+\tfrac{1}{2}\left[(E_s-E_p)^2+36H_{sp}^2\right]^{\tfrac{1}{2}}, \quad \sigma_1'=\beta s_B-\alpha p_{A+}, \quad \beta s_A-\alpha p_{B-}$$

$$E_2'=E_p-3H_{pp}', \quad \sigma_2'=(p_{A-}-p_{B+})/2^{\tfrac{1}{2}}.$$

where E_s and E_p are one-electron Hamiltonian integrals for the
2s and 2p atomic functions, H_{sp} and H_{pp}' are Hamiltonian
integrals between neighboring atoms. They are denoted as
$E(s)$, $E(p)$, $H(sp)$ and $H(\bar{p}\bar{p})$ by Lomer.[3] These parameters are
all negative. The mixing coefficients α and β between the 2s
and 2p functions are given by:

$$\alpha =-3H_{sp}/C, \quad \beta=\left\{(E_s-E_p)+\left[(E_s-E_p)^2+36H_{sp}^2\right]^{\tfrac{1}{2}}\right\}/2C \tag{8}$$

where the normalization constant C is chosen such that $\alpha^2+\beta^2=1$.

The second functions of σ_1 and σ_1' do not contribute to CS of atom A since there is no angular momentum associated with the atomic s_A functions. The $\sigma_1\sigma_1'$ and $\sigma_2\sigma_2'$ excitations would contribute to δ_z. The $\sigma_1\pi'$, $\sigma_2\pi'$, $\pi\sigma_1'$ and $\pi\sigma_2'$ excitations would contribute to δ_x. In the AE approximation, we get

$$\delta_z=(5200)\left[(E_1'-E_1)^{-1}\langle\sigma_1|L_z^{~2}|\sigma_1\rangle+(E_2'-E_2)^{-1}\langle\sigma_2|L_z^{~2}|\sigma_2\rangle\right]$$

$$=(2600)\left[2\beta^2(E_1'-E_1)^{-1}+(E_2'-E_2)^{-1}\right] \tag{10}$$

$$\delta_x=(5200)\left[(E_\pi-E_1)^{-1}\langle\sigma_1|L_x^{~2}|\sigma_1\rangle+(E_\pi-E_2)^{-1}\langle\sigma_2|L_x^{~2}|\sigma_2\rangle+(E_1'-E_\pi)^{-1}\langle\pi|L_x^{~2}|\pi\rangle\right.$$

$$=(2600)\left[\beta^2(E_\pi-E_1)^{-1}+\tfrac{1}{2}(E_\pi-E_2)^{-1}+(E_1'-E_\pi)^{-1}\right] \tag{11}$$

In the FE approximation, we get

$$\delta_z=(5200)\left[(E_1'-E_1)^{-1}|\langle\sigma_1|L_z|\sigma_1'\rangle|^2+(E_2'-E_2)^{-1}|\langle\sigma_2|L_z|\sigma_2'\rangle|^2\right]$$

$$=5200\alpha^2\beta^2(E_1'-E_1)^{-1}+1300(E_2'-E_2)^{-1} \tag{12}$$

$$\delta_x=(5200)\left[(E_\pi'-E_1)^{-1}|\langle\sigma_1|L_x|\pi'\rangle|^2+(E_\pi'-E_2)^{-1}|\langle\sigma_2|L_x|\pi'\rangle|^2\right.$$

$$+(E_1'-E_\pi)^{-1}|\langle\pi|L_x|\sigma_1'\rangle|^2+(E_2'-E_\pi)^{-1}|\langle\pi|L_x|\sigma_2'\rangle|^2$$

$$=(1300)\left[\beta^2(E_\pi-E_1)^{-1}+\tfrac{1}{2}(E_\pi-E_2)^{-1}+\alpha^2(E_1'-E_\pi)^{-1}+\tfrac{1}{2}(E_2'-E_\pi)^{-1}\right. \tag{13}$$

For corner P, energy band calculations[20,21] gives $E_1=-22$, $E_2=-20$, $E_\pi=E_\pi'=-9$, $E_1'=5$ and $E_2'=16$ eV. In addition, it is necessary to evaluate the mixing coefficients α and β. An estimate of $E_p=-6$ may be obtained by averaging the σ and σ' energies at the center Γ of BZ. From the values of E_1 and E_1', we get $E_s=-11$ and $H_{sp}=-4.4$. Substitution into (8) gives

$\alpha = 0.76$ and $\beta = 0.65$ which are consistent with the estimate $\alpha^2 = \beta^2 = 0.5$ or $\alpha = \beta = 0.71$ of Zunger[21]. From (10) to (13), we get $\delta_z = 189$, $\delta_x = 426$, $\delta_a = -237$ for the AE approximation and $\delta_z = 82$, $\delta_x = 177$, $\delta_a = -95$ for the FE approximation.

For the symmetry point Q at the midpoint of the edge of BZ, a similar calculation gives $\delta_z = 242$, $\delta_x = 446$, $\delta_a = -204$ for the AE approximation and $\delta_z = 94$, $\delta_x = 163$, $\delta_a = -69$ for the FE approximation. On averaging over the entire BZ, we get the average values $\delta_a = -170$ and -70 for the AE and FE approximations respectively.

For GICA, the net effect of the charge transfer is the partial removal (usually several per cent) of the valence π-electrons near the corner P of the BZ. This charge transfer has no effect on δ_z since contributions to δ_z comes from the $\sigma\sigma'$ excitations which are independent of the π-bands. The effect on δ_x is also small. With the partial removal of the π-electrons, there is less $\pi\sigma'$ excitation. However, the π-band is now partially vacant, hence some $\sigma\pi$ excitations are also possible. There is considerable cancellation between these two contributions since the π and π' bands are close together near the corner P. Similarly, the charge transfer effects on both δ_z and δ_x may also be small for GICD.

In summary, the "band" contributions to δ_x and δ_z come from the entire BZ and are independent of charge transfer and other detailed features of the energy bands. We have found that δ_a is between -170 and -70. These results are in general agreement with the experimental data on graphite and GICA (nearly universal values of $\delta_x \sim 180$ relative to TMS and $\delta_a \sim -140$). We note that it is very difficult to determine δ_z of pure graphite experimentally

because of the weak signals; the available experimental data[8-10,13,14] are not consistent with each other and further work is needed.

We will now consider the "dipolar" contributions to CS which may be important for GICD. Knight shift measurements[23,24] indicate that there is considerable mixing between the metal conduction electrons and the carbon $2p\pi$-electrons. The CS would come from the dipolar magnetic fields at the nuclear site due to the spin-polarized π-orbitals in the presence of the external magnetic field $\underset{\sim}{B}$. For $\underset{\sim}{B}$ parallel to the z-axis, we have $\delta_z = (\eta\chi/N) \langle r^{-3} \rangle_{2p} \langle 3\cos^2\theta - 1 \rangle$ where N is the Avagadro's number, η is the fraction of the polarized electrons that reside on carbon atoms, χ is the Pauli spin suceptibility in cm^3/mole and θ is the azimuthal angle for the π-orbital of the carbon atom. The first pair of angular brackets is radial averaging over the carbon atom π-orbital whereas the second pair is angular averaging. Since the angular dependence of the π-orbital wave function is given by $\cos\theta$, we get

$$\langle 3\cos^2\theta - 1 \rangle = \int_0^\pi \cos^2\theta(3\cos^2\theta - 1)\sin\theta \, d\theta / \int_0^\pi \cos^2\theta \sin\theta \, d\theta = 4/5. \quad (14)$$

Hence $\delta_z = (4/5)(\eta\chi/N) \langle r^{-3} \rangle_{2p}$. Because of the axial symmetry of π-orbitals about the z-axis, it follows that $\delta_x = -\delta_z/2$. Thus the "dipolar" contribution to CS anisotropy is

$$\delta_a = \delta_z - \delta_x = (6/5)(\eta\chi/N)\langle r^{-3} \rangle_{2p} \quad (15)$$

where $\langle r^{-3} \rangle_{2p} = 12.2 \, \text{Å}^{-3}$. Because of the close proximity of π-orbital to the carbon nucleus, δ_a is enhanced by approximately a factor of $v \langle r^{-3} \rangle_{2p} \sim 100$ (where $v \sim 9 \, \text{Å}^3$ is the crystal volume per carbon atom) over the Pauli contribution to the dimensionless volume susceptibility. The experimental susceptibility is the sum of several contributions[25], thus the identification of a relatively

small Pauli component may be somewhat uncertain.

We note that the presence of the metallic electrons are also clearly demonstrated by the electronic specific heat[11,26] which is proportional to temperature with the proportionality constant γ. This constant is nearly proportional to the metal concentration and may be related to the Pauli spin susceptibility χ.[25]

$$\chi = (3/\pi^2)(\mu/k_B)^2 \gamma \qquad (16)$$

where μ is the Bohr magneton, k_B is the Boltzmann constant, γ is in units of $erg(mole)^{-1}(^{\circ}K)^{-2}$ and χ is in units of $cm^3 mole^{-1}$. Thus the Pauli susceptibility χ may be eliminated between eq. (15) and (16). The result is $\delta_a = 333 \gamma \eta$ when δ_a is expressed in ppm and γ in units of $(mJ)(mole)^{-1}(^{\circ}K)^{-2}$. By combining with the experimental value of the "band" contribution $\delta_a = -140$ which is independent of intercalant concentration, we get

$$\delta_a = -140 + 333 \gamma \eta \qquad (17)$$

Using the experimental values[11,26] of γ, we have calculated δ_a from (17) and have compared with some of the experimental values[8-16] in the following table for the first and second stage GICD with the general composition $C_x K$ and $C_x Cs$. From the Knight shift data on Cs, it is plausible that the polarized electrons are shared equally between the carbon and metal atoms, hence we have identified η with the mole fraction of carbon atoms in GIC, $\eta = x/(x+1)$. The agreement is satisfactory. The variation in δ_i (isotropic part of CS with TMS as reference) is about a factor of 10 smaller than the anisotropic part δ_a. This isotropic term is usually ascribed to polarizations of the carbon core s-electrons by the unpaired π-electron spins[27], and the factor of 10 reduction has been previously observed for similar atoms.[28] The results for

GICA are also included for comparison. Very small values of γ have been observed for these compounds, hence δ_a comes from the "band" contribution only.

	GICA	C_8K	$C_{24}K$	C_8Cs	$C_{36}Cs$
γ , mJ mol^{-1}K^{-2}	0	0.697	0.241	0.63	0.19
η		8/9	24/25	8/9	36/37
δ_a, calc.	-140	66	-63	46	-79
δ_a, exptl.	-140	57	-63	35	-93
δ_i, exptl.	133	113	121	107	123

Alternatively, the choice $\eta = 1$ may be inferred from the x-ray photoelectron data[29,30] which have indicated almost complete charge transfer of metallic electrons to carbon atoms. From (17), the calculated δ_a will be changed only slightly (about 20 ppm for C_8K and C_8Cs, 3 ppm for higher stage compounds) and the agreement with experimental data is still satisfactory.

In conclusion, the CS in GIC may be expressed as the sum of "band" and "dipole" contributions. The "band" term is determined by the gross features of the two-dimensional band structure and is independent of the intercalant concentration. The "dipole" term is due to the mixing between metal and carbon electrons and is absent for GICA. It is related to the electronic specific heat for GICD. There is general agreement with the experimental data.

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